

# PATENT SPECIFICATION

419,941



Application Date: May 13, 1933. No. 13,985 / 33.

Complete Left: May 10, 1934.

Complete Accepted: Nov. 13, 1934.

## PROVISIONAL SPECIFICATION.

### Treatment of Leather.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company incorporated under the laws of Great Britain and GEORGE STUART JAMES WHITE, and HENRY ALFRED PIGGOTT, both of Hexagon House, Blackley, Manchester, a British Subject, do hereby declare the nature of this invention to be as follows:—

We have found that the properties of a grain leather as regards dyeing or staining with acid, basic or direct dyestuffs may be altered by pre-treatment with an aqueous solution of a quaternary ammonium compound containing a saturated or unsaturated aliphatic chain of not less than 10 carbon atoms. Thus a grain leather, only part of which has been so treated, when immersed in a dye-bath, shows different shades on the treated and untreated portions.

Generally the treated portion shows much less affinity, or even negligible affinity for the colour, while in a few cases the treated portion shows only a slightly less affinity. Also in some cases it takes up the colour to a different hue.

Nigrosine G (Colour Index No. 865), Naphthalene Black 12B (Colour Index No. 246), Lissamine Green SF (Colour Index No. 670) are colours for which the treated leather shows markedly less affinity; Naphtharene Orange G (Colour Index No. 27), Croceine Scarlet 3B (Colour Index No. 252), and Tartrazine N (Colour Index No. 640) are colours for which the treated leather shows only slightly less affinity. The behaviour of any particular colour can be simply ascertained by brushing a solution of the colour on to a test portion of leather, part of which has been pre-treated with the quaternary salt.

According to the present invention we obtain new and valuable coloured effects on leather by treating the leather at least on the grain side with an aqueous solution of a quaternary ammonium compound containing a saturated or unsaturated aliphatic chain of not less than 10 atoms of carbon, and then dyeing or staining with an aqueous solution of an acid, direct or basic dyestuff.

[Price 1/-]

Examples of suitable quaternary ammonium compounds are:—dodecyl trimethylammonium chloride, cetyl trimethylammonium chloride, octadecyl pyridinium iodide, stearyl pyridinium bromide, stearamidophenyltrimethyl ammonium sulphate and methylcetyl-piperidine methyl sulphate.

In carrying the invention into practical effect very diverse methods may be used. Thus leather may be sprayed, stencilled or printed with an aqueous solution of the long chain quaternary ammonium compound, then dyed by brushing, spraying, immersion or over-printing with either a solution of an individual dyestuff or a mixture of dyestuffs, especially interesting effects being obtained by using dyestuffs for which the treated leather shows different affinities as described above. In the pre-treating of suede leathers the quaternary ammonium compound is applied as a cold or warm (45° C) aqueous solution by immersing the leather. This is followed by a rinsing with cold water and dyeing in the usual manner with acid, basic or direct dyestuffs or mixtures of these. In this way it is possible substantially to prevent the generally undesirable dyeing on the grain side.

The invention is illustrated but not limited by the following examples.

#### EXAMPLE 1.

Dry skivers (Sumac grain sheepskin splits) are sprinkled with a 1% solution of stearyl pyridinium bromide. When the spots are dry the leathers are dyed by immersion in a water solution of a mixture of Nigrosine G crystals (Colour Index No. 865) and Croceine Scarlet 3B (Colour Index No. 252). The skins are then struck out and dried in the usual manner and finally an aqueous season applied to the dry leathers if desired. The skivers show scarlet spots on a black background.

#### EXAMPLE 2.

Sheepskins previously dyed with Orange II (Colour Index No. 27) are spray-stencilled with a 1% solution of trimethylcetyl ammonium chloride and dried. The leather is then sprayed with a solution of Cardinal Red J (Colour Index No.

Price 4s 6d

**BEST AVAILABLE COPY**

176) dried and finished in the usual manner. The skins show orange spots on a brown ground.

EXAMPLE 3.

5 100 lb. dry semichrome Persian suedes are treated by immersion for 30 minutes in a solution of 1% octadecylpyridinium iodide in 10 gallons of water circulating in a drum. The leathers are then rinsed 10 with cold water for 10 minutes and drummed in a warm solution of 4% Lissamine Green SF (Colour Index No.

670) calculated on the weight of the leather. After rinsing, fatliquoring and drying out in the usual manner, the shade on the suede side is found to be 15 much stronger than that obtained without the pre-treatment.

Dated the 13th day of May, 1933.

E. A. BINGEN,  
Imperial Chemical House, Millbank,  
London, S.W. 1,

Solicitor for the Applicants.

COMPLETE SPECIFICATION.

Treatment of Leather.

We, IMPERIAL CHEMICAL INDUSTRIES 20 LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company incorporated under the laws of Great Britain, GEORGE STUART JAMES WHITE, and HENRY ALFRED PIGGOTT, both 25 of Hexagon House, Blackley, Manchester, both British Subjects, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described 30 and ascertained in and by the following statement:—

We have found that the properties of vegetable-tanned leather as regards dyeing and staining with acid, basic or direct 35 dyestuffs may be altered by pre-treatment with an aqueous solution of a quaternary ammonium salt containing a saturated aliphatic chain of not less than 10 carbon atoms but no alcoholic group.

40 The alteration in properties depends to some extent on the means by which the leather is treated with the solution. When the solution is brought into contact with the leather by spraying, stencilling, 45 printing or like means, the treated portion generally shows much less affinity for the dyestuff, while in some cases it shows negligible affinity. When the solution is brought into contact with the 50 leather by an immersing operation, for instance by a drumming, the leather may show an increased affinity for the dyestuff. According to either way of bringing the solution into contact the treated 55 leather may take up the colour to a different hue.

Nigrosine G (Colour Index No. 865), Naphthalene Black 12B (Colour Index No. 246), Lissamine Green SF (Colour 60 Index No. 670) are dyestuffs for which the leather shows markedly less affinity when treated by the spraying type of operation; Orange II (Colour Index No. 151) Crocein Scarlet 3B (Colour Index 65 No. 252) and Tartrazine N (Colour Index

No. 640) are dyestuffs for which the treated leather shows only slightly less affinity when treated by the same operation. The behaviour of any particular dyestuff can be easily ascertained by applying a solution of the colour to a test portion of vegetable-tanned leather, part of which has been suitably pre-treated with the salt.

70 According to the present invention we obtain new and valuable effects on leather (which has been tanned by means of vegetable agents exclusively or in part) by pre-treating the leather in whole or in part with an aqueous solution of a quaternary ammonium salt containing a saturated aliphatic chain of not less than 10 atoms of carbon but free from hydroxyl groups and then if desired dyeing or staining with an aqueous solution of an acid, direct, or basic dyestuff.

75 Examples of suitable quaternary ammonium salts are:—dodecyltrimethylammonium chloride (from dodecyl chloride and trimethylamine) cetyltrimethylammonium chloride, octadecylpyridinium iodide (see British Patent No. 379,396), stearylpyridinium bromide (see British Patent No. 379,396), stearamido-phenyltrimethylammonium methyl sulphate (made by condensing asymmetrical dimethyl - *p* - phenylenediamine with stearoyl chloride and then treating the condensation product with dimethyl sulphate and methylcetyl piperidinium 80 methyl sulphate (made by interacting 2-molecules of N-methylpiperidine with 1 molecule of cetyl bromide, separating the cetyltrimethylpiperidine and treating with dimethyl sulphate).

85 In carrying the invention into practical effect very diverse methods may be used. Thus leather may be sprayed, 90 stencilled or printed with an aqueous solution of the salt, then if desired, dyed 95 by brushing, spraying, immersing or over-printing with either a solution of an 100

105

110

individual dyestuff or a mixture of dyestuffs, especially interesting effects being obtained by using dyestuffs for which the treated leather shows different affinities 5 as described above. In the pre-treating of vegetable-tanned suede leathers the salt is applied as a cold or warm aqueous solution by immersing the leather; this is followed by a rinsing with cold water 10 and dyeing in the usual manner if desired with acid, basic, or direct dyestuffs or mixtures of dyestuffs of any of these types.

Our treatment is distinguished from that of Specification 294,890 which 15 describes a similar treatment of animal materials including chrome-tanned leather in that we treat vegetable tanned leather. Similar treatment of chrome-tanned leather does not give the desired effect in 20 the subsequent dyeing.

The invention is illustrated but not limited by the following Examples, in which the parts are by weight.

**EXAMPLE 1.**

25 Dry skivers (Sumac grain sheepskin splits) are sprinkled with a 1% solution of stearylpyridinium bromide. When the spots are dry the leathers are dyed by immersion in a water solution of a mixture of Nigrosine G crystals (Colour Index No. 865) and Crocein Scarlet 3B (Colour Index No. 252). The skins are then struck out and dried in the usual manner and finally an aqueous season 30 applied to the dry leathers if desired. The skivers show scarlet spots on a black background.

**EXAMPLE 2.**

Vegetable tanned sheepskins previously 40 dyed with Orange II (Colour Index No. 151) are spray-stencilled with a 1% solution of trimethylcetyl ammonium chloride and dried. The leather is then sprayed with a solution of Cardinal Red (Colour 45 Index No. 176) and dried and finished in the usual manner. The skins show orange spots on a brown ground.

**EXAMPLE 3.**

100 lbs. dry semichrome Persian suedes 50 are treated by immersion for 30 minutes in a solution of 1% octadecylpyridinium iodide in 10 gallons of water circulating in a drum. The leathers are then rinsed

with cold water for 10 minutes and drummed in a warm solution of 4% 55 Lissamine Green SF (Colour Index No. 670) calculated on the weight of the leather. After rinsing, fatliquoring and drying out in the usual manner, the shade on the suede side is found to be much stronger than that obtained without the pre-treatment.

It is understood that the term leather as used in this specification and the claims does not include furs.

It is also to be noted that the process of our invention is not a fat liquoring process and does not contemplate the application of water insoluble oils.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that subject to the foregoing disclaimer what we claim is:—

1. The process for the production of new and valuable effects on leather (which has been tanned by means of vegetable agents exclusively or in part), which comprises pre-treating the leather in whole or in part with an aqueous solution of a quaternary ammonium salt, such salt containing a saturated aliphatic chain of not less than 10 atoms of carbon but no hydroxyl group, and then if desired dyeing or staining with an aqueous solution of an acid, direct, or basic dyestuff.

2. Process as claimed in Claim 1. in which the salt is a cetyltrimethylammonium halide, or a cetylpyridinium halide.

3. Process for the production of new and valuable colour effects on leather, substantially as described in each of the foregoing Examples.

4. Coloured leather, whenever manufactured by the process claimed in any of the preceding claims, or by the obvious chemical equivalent of such process.

Dated the 10th day of May, 1934.

E. A. BINGEN,  
Imperial Chemical House, Millbank,  
London, S.W. 1,  
Solicitor for the Applicants.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcomson, Ltd.—1934.

**BEST AVAILABLE COPY**